Supplementary data for the article:

Malenov, D. P.; Dragelj, J. L.; Janjić, G. V.; Zarić, S. D. Coordinating Benzenes Stack Stronger than Noncoordinating Benzenes, Even at Large Horizontal Displacements. *Crystal Growth and Design* **2016**, *16* (8), 4169–4172. https://doi.org/10.1021/acs.cgd.5b01514

SUPPORTING INFORMATION

CSD SEARCH DETAILS – defining organometallic sandwich and half-sandwich compounds

In this work, structures containing organometallic sandwich and half-sandwich compounds with benzene as one of the ligands were searched in the CSD. Only transition metals can form these organometallic compounds, while other metals (the most important example being potassium ion, K^+) form cation$\cdots\pi$ interactions.

Namely, the difference between metal radii of K^+ (1.52 Å) and Cr (1.40 Å) is 0.12 Å, while the difference in metal-centroid distance in their contacts with benzene is 1.25 Å (K^+-centroid distance is about 2.95 Å, e.g. in Fedushkin I. L. et al. , C. R. Chimie 2010, 13, 584–592, while Cr-centroid distance is 1.60 Å, e.g. in bis(benzene)chromium(0) in Haaland A., Acta Chem. Scand. 1965, 19, 41-46). Also, the binding energy in bis(benzene)chromium(0) is -61.4 kcal/mol (theoretical) or -65.5 kcal/mol (experimental) (Rayon V. M. Organometallics 2003, 22, 3304-3308), while the energy of contact between benzene and K^+ is -19.2 kcal/mol (Sunner J., Nishizawa K., Kebarle P. J. Phys. Chem. 1981, 85, 1814-1820). Therefore, the contacts of transition and non-transition metals with benzene are quite different in nature – transition metals bond covalently to benzene, forming sandwich and half-sandwich compounds, while non-transition metals form cation-pi interactions. The CSD recognizes these metal-benzene bonds in sandwich and half-sandwich compounds as metal-carbon bonds (η^6-coordination), while the contacts of non-transition metals and benzene, due to much larger distances, are not recognized as bonds while using Conquest.

In order to find benzene sandwich and half-sandwich compounds in the CSD, two approaches may be applied:

a) benzene molecule can be drawn and 3D parameter T4 (4 bonded atoms, of which one will be H, two will be C and one will be transition metal) can be added to all carbon atoms (595 hits)
b) benzene molecule can be drawn and then transition metal bonded to all carbon atoms (bond type „any“) can be added (555 hits).

The difference in number of hits originates from the compounds of Bi, Sm, K, Na and other non-transition metals, with somewhat shorter metal-centroid distances, which undoubtedly form noncovalent interactions with benzene – their metal-centroid distances are mostly around 3.0 Å, while in organometallic compounds of, for example, ruthenium, metal-centroid distances are around 1.6 Å, similar to chromium. Also, some number of structures are with transition metals, but not with η^6-coordination. Therefore, the search described in b) gives more precise set of structures, and is therefore used in the search for parallel interactions of coordinating benzene molecules.

Crystal structures archived in the CSD (version 5.37, November 2015) were searched for contacts between two (η^6) coordinating benzene molecules with parallel orientation (angle between benzene ring planes smaller than 10°). Initially, the search yielded contacts between

two coordinating benzene molecules with distance *d* between their centers lower than 8.0 Å. The contacts were considered interactions if they are within the area corresponding to the ellipsoid defined by offset *r* of 7.5 Å and normal distance R of 4.0 Å. In order to avoid contacts where metal strongly influences interactions (Figure S1b-e), additional parameters were used – angles M_1-Ω_1-Ω_2, M_2-Ω_2-Ω_1, M_1-Ω_1-M_2 and M_2-Ω_2-M_1 should all be larger than 90 °. If metal of one molecule directly interacts with benzene of other molecule, at least one of these angles is smaller than 90 ° (Figure S1b-e).

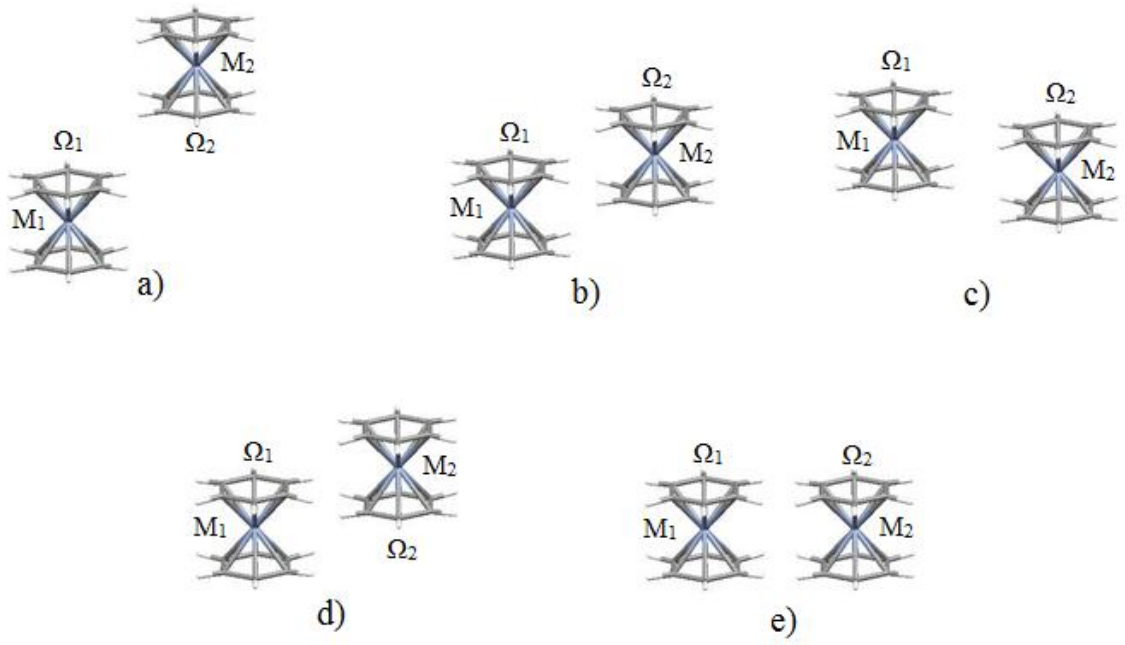


Figure S1. **a)** Interaction between two coordinating benzenes where metal of one molecule does not interact with benzene of other molecule (M_1-Ω_1-Ω_2, M_2-Ω_2-Ω_1, M_1-Ω_1-M_2 and M_2-Ω_2-M_1 angles are all larger than 90 °); **b)-e)** interactions strongly influenced by metal – in **b)** M_2-Ω_2-Ω_1 and M_2-Ω_2-M_1 are smaller than 90 °, in **c)** M_1-Ω_1-Ω_2 and M_1-Ω_1-M_2 are smaller than 90 °, in **d)** M_1-Ω_1-Ω_2 and M_2-Ω_2-Ω_1 are smaller than 90 °, in **e)** M_1-Ω_1-M_2 and M_2-Ω_2-M_1 are smaller than 90 °

The contacts depicted at Figure S1b-e were therefore not included in this study, i.e. only contacts at Figure S1a are considered parallel interactions of coordinating benzenes that are not directly influenced by metals.

STRUCTURES OF MONOMERS

Eclipsed and staggered conformations of both complexes were fully optimized at TPSS-D2/def2-TZVP level of theory and confirmed as true minima by performing calculations of vibrational frequencies. It was shown that staggered conformation of (benzene)tricarbonylchromium was more stable than eclipsed by the value of 0.27 kcal/mol,

and eclipsed conformation of *bis*(benzene)chromium was 1.14 kcal/mol more stable than staggered. Therefore, staggered (benzene)tricarbonylchromium and eclipsed *bis*(benzene)chromium were used for calculations of energies of parallel interactions of coordinated benzene molecules (Figure 3 in the main text).

INTERACTION ENERGIES AT DFT LEVEL WITH AND WITHOUT DISPERSION CORRECTION

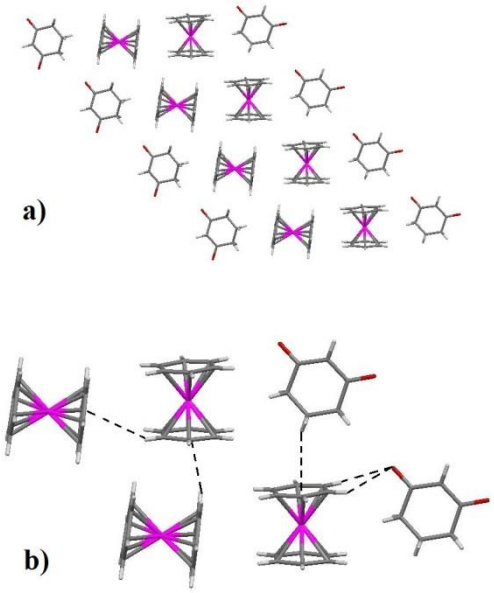
The origin of interaction energies at r = 1.5 Å and r = 5.0 Å was roughly evaluated by performing additional calculations at TPSS level, which does not include dispersion component. It was found that interactions are calculated to be repulsive if dispersion is not included, the stronger repulsion at r = 1.5 Å being in half-sandwich||half-sandwich system (Table S1). This also implied that the dispersion contribution is higher in this system. However, at r = 5.0 Å both dispersion and DFT terms are reduced for the same percentage, compared to the system at r = 1.5 Å (Table S1). On the other side, the repulsive DFT (dispersion-free) term in sandwich||sandwich system is reduced by almost 80%, resulting in only 20% of reduction of the overall interaction energy, since dispersion is reduced by approximately 50% (Table S1). This results in sandwich||sandwich interactions being remarkably strong at large offset values, and much stronger than half-sandwich||half-sandwich interaction.

Table S1. TPSS dispersion corrected DFT energies (DFT-D), dispersion-free DFT energies (DFT) and dispersion correction values (D) for benzene||benzene half-sandwich||half-sandwich and sandwich||sandwich model systems at r = 1.5 Å and r = 5.0 Å. % denotes the percentage of energies at r = 5.0 Å in comparison to the strongest interaction energies (at r = 1.5 Å, 100%). All energies are given in kcal/mol.

MODEL-SYSTEM	r = 1.5 Å			r = 5.0 Å					
	DFT-D	D	DFT	DFT-D	%	D	%	DFT	%
benzene||benzene	-2.76	-5.66	2.90	-2.05	74	-2.60	46	0.55	19
half-sandwich||half-sandwich	-3.29	-8.12	4.83	-1.27	39	-3.19	39	1.92	40
sandwich||sandwich	-3.69	-7.48	3.79	-3.03	82	-3.89	52	0.86	23

SUPRAMOLECULAR STRUCTURE FOR SANDWICH||SANDWICH INTERACTIONS

In crystal structure ZUXCAW01[1], parallel interaction between two benzenes of *bis*(benzene)chromium molecules is formed at offset value of r = 5.083 Å, leaving uncoordinated faces of both benzenes available for the formation of additional interactions (Figure S3a). This way sandwich compounds form additional interactions with other (large) molecules: C-H/π interactions with other molecules of *bis*(benzene)chromium (both as π-donor and π-acceptor), and C-H/π and C-H/O interactions with 1,3-cyclohexanedionate (Figure S3b). In crystal structure GOPKIF[2], coordinated benzene molecules interact with offset value of r = 1.19 Å, since methyl-chromate is not as voluminous as 1,3-cyclohexanedionate and *bis*(benzene)chromium, and thus could not fill the gap if interaction with large offset would be formed (Figure S4).



[1] D. Braga, A. L. Costa, F. Grepioni, L. Scaccianoce, E. Tagliavini, Organometallics (1997), 16, 2070
[2] D. Braga, F. Grepioni, E. Tagliavini, J. J. Novoa, F. Mota, New J. Chem. (1998), 22, 75

Figure S2. Fragment of crystal structure ZUXCAW01 (a) and additional interactions formed due to the formation of parallel interaction with large horizontal displacement of coordinated benzene molecules (b)

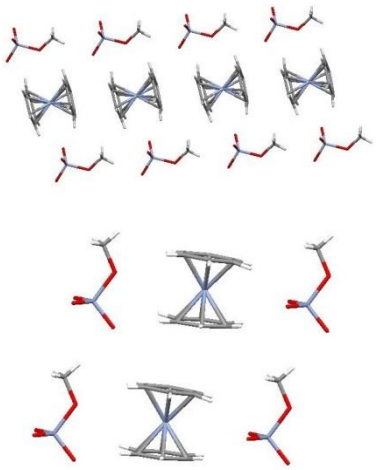


Figure S3. Fragment of crystal structure GOPKIF